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COSMOCHEMISTRY APPLIED TO MAJOR PLANETARY  
INTERIORS: EXPERIMENTAL STUDIES Status  
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HIGH PRESSURE COSMOCHEMISTRY APPLIED TO  
MAJOR PLANETARY INTERIORS: EXPERIMENTAL STUDIES

Investigators

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SUMMARY

The overall objective of this project is to determine the properties and boundaries of several high pressure phases of the  $H_2$ -He- $H_2O$ - $NH_3$ - $CH_4$  system that are needed to constrain theoretical models of the interiors of the major planets. This is one of the first attempts to measure phase equilibria in binary fluid-solid systems in diamond anvil cells and, in that respect, represents an attempt to advance the state of modern high-pressure experimentation. Vibrational spectroscopy of materials confined in externally heated cells is our primary experimental probe. The spectroscopy is supplemented by direct visual observation and x-ray diffraction crystallography. We also are measuring adiabats of these materials which provide constraints for models of heat flow in these bodies.

Our initial efforts involve the  $NH_3$ - $H_2O$  binary. This system is especially relevant to models for surface reconstruction of the icy satellites of Jupiter and Saturn. It also is relatively easy to handle and helps us to identify technical problems so that we can solve them before we add more volatile components. During the period covered by this report (5/83-11/83), work continued on the P-T-X diagram for  $0 \leq X \leq 0.50$ , and on the development of techniques for measuring adiabats of phases of  $NH_3$ - $H_2O$ .

Detailed Description of Work in Progress During the Period 5/1/83-10/31/83  
 NASA Grant NAGW-104

Phase Diagram of  $\text{NH}_3 \cdot \text{H}_2\text{O}$

Ms. Schwake's work on the phase diagram of 1:1  $\text{NH}_3 \cdot \text{H}_2\text{O}$  has been described in earlier reports. During the last six months, Dr. Johnson extended this work to compositions in the range  $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$ ,  $0 \leq x \leq 0.3$ , at pressures up to 4 GPa at room temperature ( $20 \pm 2^\circ\text{C}$ ). Phases were identified visually using a microscope and polarized optics; pressures were determined by the ruby luminescence method. For low-ammonia compositions ( $x \leq 0.15$ ), the following assemblages succeed one another as pressure increases: liquid; liquid plus Ice VI (at 1.0+ GPa, composition dependent); liquid plus Ice VII (at 2.1 GPa); Ice VII plus  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (at 3.5 GPa). When  $x$  is greater than 0.15, the water ice plus liquid fields are replaced by the  $\text{NH}_3 \cdot 2\text{H}_2\text{O}$  plus liquid field, which is stable between 0.7 and 2.4 GPa.

Compositions of the ammonia ices were determined by estimating relative amounts of water and ammonia ices at known compositions. The  $\text{NH}_3 \cdot \text{H}_2\text{O}$  phase is strongly anisotropic, has a refractive index much lower than that of Ice VII, and cracks in two nonperpendicular networks.  $\text{NH}_3 \cdot \text{H}_2\text{O}$  has a refractive index close to that of Ice VII and does not crack readily. Both phases are colorless.

From Andrea Schwake's data for  $\text{NH}_3 \cdot \text{H}_2\text{O}$  [unpublished] and published data for  $\text{H}_2\text{O}$  [Mishima and Endo, 1980] and the  $\text{NH}_3 \cdot \text{H}_2\text{O}$  system at 1 bar [Rollet and Vuillard, 1956], a liquidus phase diagram can be constructed in P-T-X space for the system  $\text{H}_2\text{O}-\text{NH}_3 \cdot \text{H}_2\text{O}$ . This is shown in Figure 1. Published data are indicated by the heavy lines. Data from this laboratory--Schwake's data (the P-T plane at  $X = 0.5$ ), data obtained from measurements of adiabats reported in the May 1983 progress report, and Dr. Johnson's data--are shown as circles. Phase boundaries are indicated as solid lines where they are taken from experiment, dashed when they are hypothesized, and dotted where the hypothetical lines pass behind other features on this phase diagram. Phases are labelled as follows:

blank circles	liquid
stripped circles	Ice VI
filled circles	Ice VII
crosshatched circles	$\text{NH}_3 \cdot 2\text{H}_2\text{O}$
dotted circles	$\text{NH}_3 \cdot \text{H}_2\text{O}$

Composition difficulties described in the May 1983 report imply that Schwake's data represent lower limits for the  $\text{NH}_3 \cdot \text{H}_2\text{O}$  melting curve, which has been drawn accordingly. The curves drawn through Johnson's data also take into account the (sometimes considerable) hysteresis seen by her. All phases represented here (Ice I, II, III, IV, VI, and VII,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $\text{NH}_3 \cdot 2\text{H}_2\text{O}$ ) also are assumed to be stoichiometric. These measurements will be described in a paper to be given at the December AGU meeting and an invited talk at the NATO Workshop on Ices in the Solar System in January.

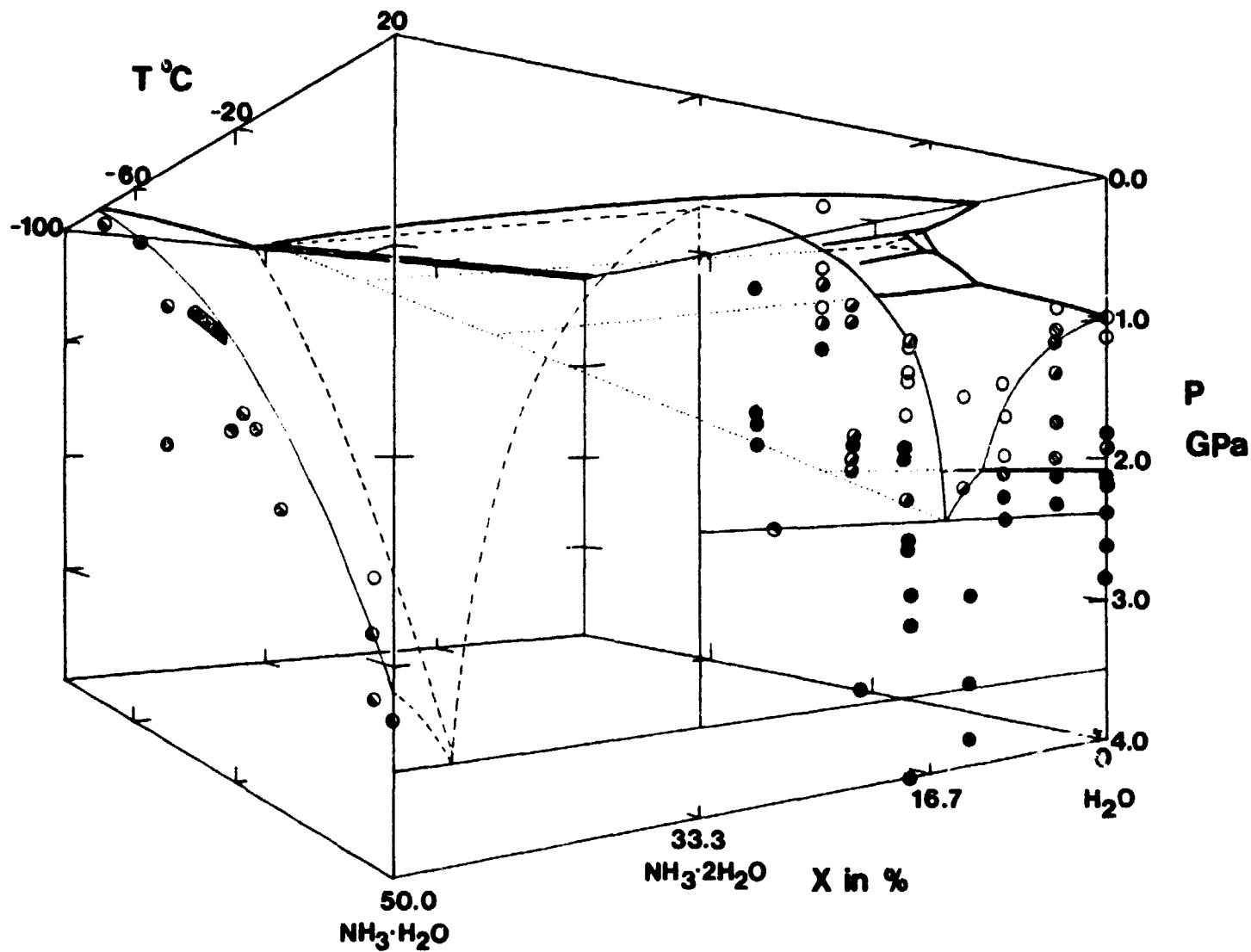


Fig. 1 Partial P-T-X diagram for the  $\text{NH}_3\text{-H}_2\text{O}$  system. The symbols and notation are explained in the text.

In the near future, we plan to extend this work in three directions: 1. The room temperature phase mapping will be extended to compositions richer in ammonia. 2. The infrared, Raman, and X-ray characterization work will be expanded in order a) to determine the structure of  $\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , b) to establish whether the  $\text{NH}_3 \cdot \text{H}_2\text{O}$  phase at high pressure is identical to the low temperature ice of the same composition, and c) to examine possible non-stoichiometry. 3. The phase mapping will be extended to other temperatures and pressures, especially near  $X = 0.33$  and  $0.67$ .

#### Infrared Spectra of Ices

Professor Wilfried Holzapfel's interest in infrared spectra of aqueous ices and our desire to develop analytical procedures for high pressure phases of the  $\text{CH}_4\text{-NH}_3\text{-H}_2\text{O}$  "ices" motivated us to develop an infrared capability during his Fall 1982 sabbatical at UCLA. This development is described in a short paper that will appear in the *J. Geophys. Res. (Red)* supplement for the proceedings of *Lunar and Planetary Science XIV*.

Dr. Johnson is now preparing to use this technique to identify coexisting phases in  $\text{H}_2\text{O-NH}_3$  mixtures. The strength of the infrared bands of these systems means that very thin samples must be used for infrared work. However, it is inconvenient to do surveys with thin samples so our approach must be to study infrared spectra of a few samples of selected compositions in order to confirm the visual observations.

#### Adiabats of $\text{H}_2\text{O-NH}_3$ Solutions at High Pressures

For several years, Dr. Reinhart Boehler of UCLA's Institute of Geophysics and Planetary Physics has measured adiabats,  $(dT/dP)_g = \alpha V T / C_p$ , of solids to pressures of the order of 5 GPa. The experiment involves measuring temperature changes which follow rapid pressure changes. Adiabats are the relevant equations of state for convecting planets, and pressure dependences of adiabats and thermal expansivities, can be used to derive the Gruneisen parameters needed to convert shock Hugoniots to isotherms.

During Spring 1983, Dr. Boehler and Professor Nicol showed how to adapt these techniques for fluid mixtures of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ; this development was described in the May 1983 report. In order to apply this method to multi-phase systems, concentrations must be carefully selected and controlled because, with the available apparatus, the composition of the part of the sample whose temperature changes cannot be determined. Many of the interesting compositions will have to be prepared as gas-liquid mixtures above atmospheric pressure and/or below room temperature. Thus, since the Summer, Ms. Schwake, Dr. Boehler, and Professor Nicol have been working to develop and to test techniques for preparing such samples.

### Personnel

Most of the work during the first two years of this grant were performed under Professor Nicol's direction by Ms. Andrea Schwake, a postgraduate physicist who had been trained in Professor Holzapfel's laboratory. Since September 1982, Ms. Schwake has been in the doctoral program of the Department of Chemistry and Biochemistry and, during this period, has had to devote much of her time to courses and other degree requirements. We expect that she will be able to resume regular participation in this project in early 1984. However, during the Summer, Andrea worked with Dr. Reinhart Boehler, an Assistant Research Geophysicist in UCLA's Institute of Geophysics and Planetary Physics, to extend the measurements of the adiabats of ammonia-water solutions reported in the May 1983 progress report.

Dr. Mary Johnson joined the research group in January 1983 and has been actively involved in the phase equilibria studies at compositions and components other than 1:1  $H_2O-NH_3$ . She obtained most of the new results reported here and is actively continuing data collection.

### References:

Mishima, O., and S. Endo, *J. Chem. Phys.* 73, 2454 (1980).  
Rollet, A.P., and G. Vuillard, *C.R. Acad. Sci., Paris*, 243 383 (1956).

### Bibliographic Data

W.B. Holzapfel, B. Seiler, and M. Nicol, "Effect of Pressure on Infrared Spectra of Ice VII", *J. Geophys. Res.* (In press). (Preprint submitted with the May 1983 report.)

M. L. Johnson, M. Nicol and A. Schwake, "Preliminary Phase Diagram for the Water-Rich Region of the System  $NH_3-H_2O$  to 4.0 GPa". Abstract of paper to be read at the December 1983 meeting of the American Geophysical Union.

M. L. Johnson, A. Schwake, and M. Nicol, "Partial Phase Diagram for the  $NH_3-H_2O$  System: The Water-Rich Region at 20 °C". Abstract of an invited talk at the NATO Symposium on Ices in the Solar System, Nice, France, January 1983.

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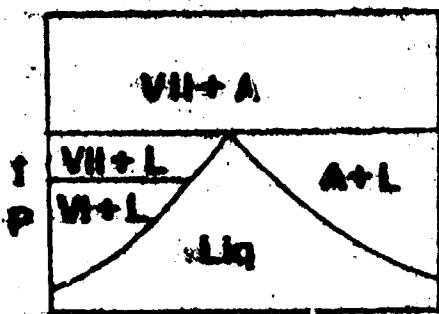
Abstract submitted for the American Geophysical Union  
Meeting, San Francisco, CA, December 1983

Preliminary Phase Diagram for the Water-Rich Region of  
the System  $\text{NH}_3\text{-H}_2\text{O}$  to 4.0 GPa

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A P-T-X phase diagram of the system  $\text{NH}_3\text{-H}_2\text{O}$  is needed in order to understand the interiors of many bodies in the solar system (Uranus, Neptune, Titan). We have used a diamond cell to compress several  $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$  compositions in the range  $x \leq 0.3$  at room temperature. Phases were identified visually, with pressures measured by the ruby fluorescence technique; phase boundaries were determined while both increasing and decreasing pressure. Three solid phases are seen. Ice VI forms as frost-like crystals (1.0 GPa at  $x = 0$ ; 2.0 GPa at  $x = 0.10$ ); nucleation is enhanced by addition of small amounts of ammonia. Ice VII forms as equant crystals from the liquid ( $x \geq 0.10$ ) or from Ice VI. The third solid, an ammonia-rich phase labelled "A", is tentatively identified with  $\text{NH}_3\cdot 2\text{H}_2\text{O}$ ; but this identification needs to be confirmed. The phase has a low refractive index contrast with the liquid and, under strain, cracks along two non-perpendicular networks.

A preliminary phase diagram is shown here. Two triple points are expected at  $x = 0.10$ ,  $P = 2.1$  GPa (Liq-VI-VII) and  $x = 0.15 \pm 0.03$ ,  $P = 2.45$  GPa (Liq-VII-A). At  $x \geq 0.22$ , A crystallizes below 1.0 GPa.



This work is supported by NASA Contract NAGW-104.

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Abstract of Invited Presentation at the Physics of Ice Session of the NATO Workshop on Ices in the Solar System, Nice, France, January 16-19, 1984

PARTIAL PHASE DIAGRAM FOR THE SYSTEM  $\text{NH}_3\text{-H}_2\text{O}$ :

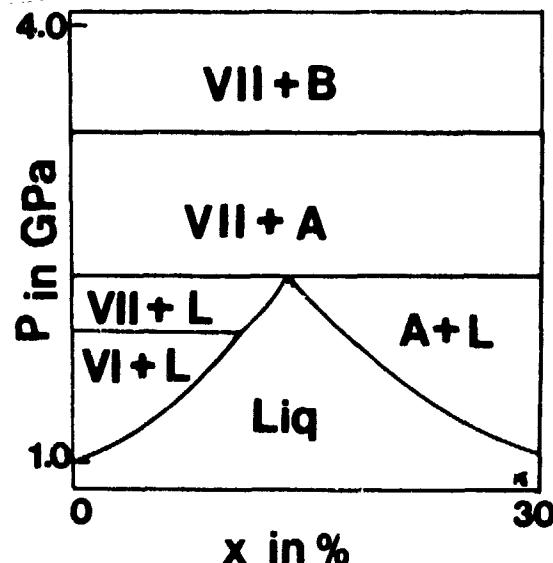
THE WATER-RICH REGION AT 20 °C

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ABSTRACT

As part of a project with the overall goal of determining phase boundaries of the  $\text{H}_2\text{O-NH}_3$  system, we have compressed  $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$  mixtures at compositions in the range,  $0 \leq x \leq 0.3$ , in diamond-anvil cells at pressures up to 4 GPa and room temperature. Other compressions have been performed at compositions,  $0.46 \leq x \leq 0.50$ , from 150 to 400 K at pressures up to 5 GPa. Phases have been identified visually with a microscope and polarized optics. The  $\text{NH}_3\cdot 2\text{H}_2\text{O}$  phase, "A" in the accompanying preliminary phase diagram, is strongly anisotropic with a much smaller refractive index than that of ice VII and cracks in two nonperpendicular networks.  $\text{NH}_3\cdot \text{H}_2\text{O}$ , "B" in the diagram, has a refractive index closer to that of Ice VII and does not appear to form cracks. Both phases are colorless. Phase boundaries were determined on both increasing and decreasing pressure, pressures were determined by the ruby luminescence method, and compositions of the ammonia ices were determined by estimating relative amounts of water and ammonia ices at known overall compositions. For low-ammonia compositions ( $x \leq 0.15$ ), the following assemblages succeed one another as pressure increases: liquid; liquid plus Ice VI (at 1.0+ GPa); liquid plus Ice VII (at 2.1 GPa); Ice VII plus  $\text{NH}_3\cdot \text{H}_2\text{O}$  (at 3.5 GPa). For  $0.15 \leq x \leq 0.30$ , the water ice plus liquid fields are replaced by the  $\text{NH}_3\cdot 2\text{H}_2\text{O}$  plus liquid field at pressures down to 1.0 GPa and lower.



This work was supported by NASA Contract NAGW-104.